

# LIGAND FIELD THEORY OF MAGNETIC SUSCEPTIBILITY AND ANISOTROPY IN $\text{CoSiF}_6 \cdot 6\text{H}_2\text{O}$

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**ABSTRACT.** We have derived an expression for the principal ionic magnetic susceptibilities  $K_{\parallel}$  ( $\parallel$  or  $\perp$ ) along and perpendicular to the trigonal axis of  $\text{CoSiF}_6 \cdot 6\text{H}_2\text{O}$  crystal, on the basis of molecular orbital theory of Stevens (1953), Bose *et al* (1960) and compared this with the experimental results by one of us (L.C.J.) The anisotropic reduction in spin-orbit coupling coefficient is due to the overlap of  $\text{Co}^{2+}$   $d$ -charge clouds with  $s$ - and  $p$ -ligand charge clouds. The increase in trigonal field coefficient  $\Delta$  below  $90^\circ\text{K}$  is due to thermal expansion or relaxation effects but the large decrease in the region of  $250^\circ\text{K}$  appears to be due to some kind of phase transition reversible in character, evidence for which is available from some of the recent measurements between  $90^\circ\text{K}$  to  $300^\circ\text{K}$  in our laboratory.

## INTRODUCTION

An octahedral field of the type  $O_h$  splits up the ground state  $3d^7\ ^4F$  of free  $\text{Co}^{2+}$  into two triplets  $^4T_1$ ,  $^4T_2$  and a singlet  $^4A_2$  of successively increasing energies, the overall separation being  $\sim 21000\text{ cm}^{-1}$  (Abragam and Pryce, 1951). There is another term  $^4T_1(^4P)$  coming out of the same configuration  $3d^7$  of the free ion which lies above  $^4T_1(^4F)$  at about  $19,800\text{ cm}^{-1}$  in the crystal (Abragam and Pryce, 1951). Abragam and Pryce (1951) have given a theory of the  $\text{Co}^{2+}$  ion in a cubic field with a small tetragonal or trigonal component to explain the paramagnetic resonance data on  $\text{Co}^{2+}$  Tutton salts and  $\text{CoSiF}_6 \cdot 6\text{H}_2\text{O}$  (Bleaney and Ingram, 1951). The effect of admixture of excited  $^4T_1(^4P)$ ,  $^4A_2$ ,  $^4T_2$  levels upon the lowest  $^4T_1(^4F)$  level in this theory, has been included through the orbital Landé  $g$  factors  $\alpha$ ,  $\alpha'$  ( $\parallel$  or  $\perp$  respectively, to the trigonal or tetragonal symmetry axis as the case may be of the  $\text{Co}^{2+}$  ion), which are appreciably different from the free ion value  $3/2$  for  $F$  state, Bose *et al* (1961) have used this theory to explain the magnetic susceptibilities of  $\text{Co}^{2+}$  Tutton salts, without introducing the effect of the overlap between the  $3d$ -orbitals of  $\text{Co}^{2+}$  and the  $s$ - and  $p$ -orbitals of the ligand atoms. In the present paper while deriving the expressions for magnetic susceptibility and

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anisotropy of the trigonally distorted  $\text{Co}^{2+}$ ,  $6\text{H}_2\text{O}$  complex the more general molecular orbital approach is followed. The susceptibility measurements of one of us (L.C.J.) on  $\text{CoSiF}_6 \cdot 6\text{H}_2\text{O}$  in the range 300 K to 1.67°K, have been used to evaluate the theoretical parameters. The salt is isomorphous to the hydrated  $\text{Fe}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  fluosilicates and is of trigonal symmetry (space gr.  $\text{C}_{3i}^2$ , Pauling 1930), with a single trigonally distorted  $[\text{Co}^{2+}, 6\text{H}_2\text{O}]$  octahedral complex in the unit cell, so that the principal ionic susceptibilities  $K_i$  ( $i = \parallel$  or  $\perp$  to the trigonal axis of the ion) are identical with the measured values  $\chi_i$  (principal gm. molecular susceptibilities) of the crystal, corrected for diamagnetism.

#### MOLECULAR ORBITAL THEORY OF TRIGONALLY DISTORTED ( $\text{Co}^{2+}$ , $6\text{H}_2\text{O}$ ) COMPLEXES

##### (a) The cubic field orbitals of ( $\text{Co}^{2+}$ , $6\text{H}_2\text{O}$ )

$\text{Co}^{2+}$  ion can be considered as a system consisting of three  $d$ -holes in the  $3d$  subshell and the several states  ${}^4T_1(F)$ ,  ${}^1T_2(F)$ ,  ${}^1A_2(F)$  and  ${}^3T_1(P)$  arise out of  $[(t_{2g})^1(e_g)^2]$ ,  $[(t_{2g})^2(e_g)^1]$ ,  $[(t_{2g})^3]$  and  $[(e_g)^1(t_{2g})^2]$  configurations respectively. The determinantal wave functions for the lowest triplet  ${}^1T_1(F)$  (considering only the orbital part) can be written as

$$\left. \begin{aligned} \psi_1 &= |e_a e_b t_a| \\ \psi_2 &= |e_a e_b t_b| \\ \psi_3 &= |e_a e_b t_c| \end{aligned} \right\} \quad \dots (1)$$

which are inclusive of the overlap of surrounding ligand  $s$ - and  $p$ -orbitals with central metal  $d$ -orbitals as given by

$$\left. \begin{aligned} t_a &= N \left[ d_{xy} + \frac{\lambda}{2} (\pi x_1 + \pi y_2 + \pi x_3 + \pi y_4) \right] \\ t_b &= N \left[ d_{yz} + \frac{\lambda}{2} (\pi x_2 + \pi y_3 + \pi x_6 + \pi y_5) \right] \\ t_c &= N \left[ d_{xz} + \frac{\lambda}{2} (\pi x_3 + \pi y_1 + \pi x_4 + \pi y_6) \right] \\ e_a &= N' \left[ dx^2 - y^2 + \frac{\lambda'}{2} (\sigma_1 + \sigma_3 - \sigma_2 - \sigma_5) \right] \\ e_b &= N' \left[ d3z^2 - r^2 + \frac{\lambda'}{2\sqrt{3}} (2\sigma_3 + 2\sigma_6 - \sigma_1 - \sigma_4 - \sigma_2 - \sigma_5) \right] \end{aligned} \right\} \quad \dots (2)$$

where  $N$ 's are normalizing constants  $\lambda$ 's are the amounts of admixtures of the  $s$ - and  $p$ -orbitals with the  $d$ -orbitals. Here all  $\sigma$ -bonds are described by using  $z$ -coordinates of the ligands and  $\pi$ -bonds by using  $x$  and  $y$  coordinates, all  $z$ -coordinates of the ligands pointing towards the metal atom (Van Vleck, 1935).

### (b) Trigonal orbitals

The appropriate trigonal orbital states for the lowest triplet of  $\text{Co}^{2+}$  complex on quantization along the trigonal axis, are

$$\left. \begin{aligned} |+\rangle &= \frac{1}{\sqrt{3}} [\omega |\psi_2\rangle + \omega^2 |\psi_3\rangle + |\psi_1\rangle] \\ |0\rangle &= \frac{1}{\sqrt{3}} [|\psi_2\rangle + |\psi_3\rangle + |\psi_1\rangle] \\ |-\rangle &= \frac{1}{\sqrt{3}} [\omega^2 |\psi_2\rangle + \omega |\psi_3\rangle + |\psi_1\rangle] \end{aligned} \right\} \quad (3)$$

where  $\omega = \exp\left(\frac{2\pi i}{3}\right)$  and  $\psi_1$  etc., are given by (1). The overlap of the surrounding ligand  $s$ - and  $p$ -orbitals with the central  $d$ -orbitals introduces two orbital reduction factors. (Griffiths, 1961) (i)  $\kappa$  within a manifold of  $t_{2g}$  orbitals (ii)  $\kappa'$  between a  $t_{2g}$  and  $e_g$  manifold. On actual calculation it is seen that so long as we are confined only to  ${}^4T_1(F)$  state of  $\text{Co}^{2+}$ , only the factor  $\kappa$  is of importance. Also in consequence of this the anisotropic reduction in  $\zeta_i$  ( $i = \parallel$  or  $\perp$  to the trigonal axis of the ion) the spin-orbit coupling parameter, from its free ion value, is mainly due to the overlap of  $p$ -orbitals with the  $d$ -orbitals.

### FINE STRUCTURE

The three states  $|+\rangle$ ,  $|0\rangle$ ,  $|-\rangle$  behave as the three orbital components of atomic  ${}^4P$  state with  $l_s' = 1, 0, -1$  respectively. The appropriate Hamiltonian for the lowest triplet state is (Bose *et al*, 1960, 1964)

$$H = V_{trig} - \alpha U_\xi S_\xi - \alpha' (U_\xi S_\xi + U_\eta S_\eta) \quad (4)$$

where  $\xi$  is a coordinate (not to be confused with  $\zeta_i$  spin-orbit coupling) along the trigonal axis of the crystal and  $\xi, \eta, \zeta$  form a mutually orthogonal right handed set of coordinates.

Operating with the above Hamiltonian upon the effective  ${}^4P$ -term and solving we get the eigen-values as follows :

$$\left. \begin{aligned} E_1 &= \alpha \zeta_{||} x_1 \\ E_2 &= \alpha \zeta_{||} x_2 \\ E_3 &= \frac{1}{2} [(\Delta - \frac{1}{2} \alpha \zeta_{||}) - \{(\Delta + \frac{1}{2} \alpha \zeta_{||})^2 + 6\alpha'^2 \zeta_{\perp}^2\}^{\frac{1}{2}}] \\ E_4 &= -\frac{3}{2} \alpha \zeta_{||} \\ E_5 &= \frac{1}{2} [(\Delta + \frac{1}{2} \alpha \zeta_{||}) + \{(\Delta + \frac{1}{2} \alpha \zeta_{||})^2 + 6\alpha'^2 \zeta_{\perp}^2\}^{\frac{1}{2}}] \\ E_6 &= \alpha \zeta_{||} x_6 \end{aligned} \right\} \quad (5)$$

where  $x_1, x_2$  and  $x_6$  are the roots of the cubic eqn.

$$x^3 - x^2(2+\delta) + \left(2\delta + \frac{3}{4} - \frac{7}{2} \rho^2\right) x - \frac{3}{4} \delta + \frac{15}{4} \rho^2 = 0$$

where

$$\delta = \frac{\Delta}{\alpha \zeta_{||}} \quad \rho = \frac{\alpha' \zeta_{\perp}}{\alpha \zeta_{||}}$$

$\Delta$  is the trigonal field separation between the split components (a doublet and a singlet) of the ground triplet  ${}^4T_1$ . The corresponding eigenstates are :

$$\left. \begin{aligned} \phi_1 &= a_1 | -1, \frac{3}{2} \rangle + b_1 | 0, \frac{1}{2} \rangle + c_1 | 1, -\frac{1}{2} \rangle \\ \phi_{1-} &= a_1 | 1, -\frac{3}{2} \rangle + b_1 | 0, -\frac{1}{2} \rangle + c_1 | -1, \frac{1}{2} \rangle \\ \phi_2 &= a_2 | -1, \frac{3}{2} \rangle + b_2 | 0, \frac{1}{2} \rangle + c_2 | 1, -\frac{1}{2} \rangle \\ \phi_{2-} &= a_2 | 1, \frac{3}{2} \rangle + b_2 | 0, -\frac{1}{2} \rangle + c_2 | -1, \frac{1}{2} \rangle \\ \phi_3 &= a_3 | 0, \frac{3}{2} \rangle + b_3 | 1, \frac{1}{2} \rangle \\ \phi_{3-} &= a_3 | 0, -\frac{3}{2} \rangle + b_3 | -1, -\frac{1}{2} \rangle \\ \phi_4 &= | 1, \frac{3}{2} \rangle \\ \phi_{4-} &= | -1, -\frac{3}{2} \rangle \\ \phi_5 &= a_5 | 0, \frac{3}{2} \rangle + b_5 | 1, \frac{1}{2} \rangle \\ \phi_{5-} &= a_5 | 0, -\frac{3}{2} \rangle + b_5 | -1, -\frac{1}{2} \rangle \\ \phi_6 &= a_6 | -1, \frac{3}{2} \rangle + b_6 | 0, \frac{1}{2} \rangle + c_6 | 1, -\frac{1}{2} \rangle \\ \phi_{6-} &= a_6 | 1, \frac{3}{2} \rangle + b_6 | 0, -\frac{1}{2} \rangle + c_6 | -1, \frac{1}{2} \rangle \end{aligned} \right\} \quad \dots \quad (6)$$

where

$$\begin{aligned}
 a_i &= \frac{\sqrt{\frac{3}{2}} \alpha' \zeta_{\perp}}{\frac{3}{2} \alpha \zeta_{\parallel} - E_i} \cdot b_i \\
 c_i &= \frac{\sqrt{2} \alpha' \zeta_{\perp}}{\frac{3}{2} \alpha \zeta_{\parallel} - E_i} \cdot b_i \\
 a_i^2 + b_i^2 + c_i^2 &= 1, \quad i = 1, 2, 6. \\
 a_j &= \frac{\sqrt{\frac{3}{2}} \alpha' \zeta_{\perp}}{\Delta - E_j} b_j \\
 a_j^2 + b_j^2 &= 1, \quad j = 3, 5
 \end{aligned} \tag{7}$$

The energy values are formally the same as in our earlier paper (Bose *et al.*, 1961) except that in the present the spin-orbit coupling coefficient in crystal is necessarily anisotropic and the effect of covalency overlap is automatically introduced in the wavefunctions operated upon by the Hamiltonian (eqn. 4).

#### EXPRESSION FOR SUSCEPTIBILITY

Calculating the effect of the magnetic perturbations  $\beta H(L+2S)$ , upto the second order, we get the expressions for principal magnetic susceptibility  $K_i$  ( $i = \parallel$  or  $\perp$  to the trigonal axis of the crystal).

In the present case these are :

$$\begin{aligned}
 K_{\parallel} &= \frac{N\beta^2}{kW} \left[ \frac{1}{T} \left\{ \sum_{i=1,2,6} G_{1z}^i \exp \left( -\frac{E_i - E_1}{kT} \right) + \sum_{j=3,5} G_{1z}^j \exp \left( -\frac{E_j - E_1}{kT} \right) \right. \right. \\
 &+ 2(3 - \alpha \kappa_{\parallel}) \exp \left( -\frac{E_4 - E_1}{kT} \right) \left. \right\} + 2k \left\{ \sum_{i,l=1,2,6} \sum_{i \neq l} \frac{S_{il}}{E_l - E_i} \exp \left( -\frac{E_i - E_1}{kT} \right) \right. \\
 &\left. \left. + 2(3a_3a_5 - \alpha k_{\parallel} b_3b_5 + b_3b_5) \left( \exp \left( -\frac{E_3 - E_1}{kT} \right) - \exp \left( -\frac{E_5 - E_1}{kT} \right) \right) \right\} \right] \\
 K_{\perp} &= \frac{N\beta^2}{kW} \left[ \frac{1}{T} \left\{ \sum_{i=1,2,6} G_{1z}^i \exp \left( -\frac{E_i - E_1}{kT} \right) \right\} \right. + 2k \left\{ G_{2z}^1 + G_{2z}^2 \exp \left( -\frac{E_2 - E_1}{kT} \right) \right. \\
 &+ G_{2z}^3 \exp \left( -\frac{E_3 - E_1}{kT} \right) + G_{2z}^4 \exp \left( -\frac{E_4 - E_1}{kT} \right) \\
 &\left. \left. + G_{2z}^5 \exp \left( -\frac{E_5 - E_1}{kT} \right) + G_{2z}^6 \exp \left( -\frac{E_6 - E_1}{kT} \right) \right\} \right] \tag{8}
 \end{aligned}$$

where

$$\begin{aligned}
 W &= 2 \sum_{i=1} \exp \left( -\frac{E_i - E_1}{kT} \right) \\
 G_{1x} &= \frac{1}{2} [ \{ 2(a_i^2 - c_i^2) \alpha \kappa_{||} + 6a_i^2 + 2b_i^2 - 2c_i^2 \} + \{ (3a_i^2 - c_i^2) v_1 + b_i^2 v_2 \\
 &\quad + (\sqrt{6} a_i b_i - \sqrt{8} b_i c_i) v_3 \}^2 ] \\
 G_{1x}^j &= 2 [ -b_j^2 \alpha \kappa_{||} + 3a_j^2 + b_j^2 ]^2 \\
 G_{1x}^i &= \frac{1}{2} \left[ \left\{ -\frac{4\alpha' \kappa_{\perp}}{\sqrt{2}} b_i c_i + 4\sqrt{3} a_i c_i + 4b_i^2 \right\} \right. \\
 &\quad \left. + \left\{ b_i^2 v_4 + c_i^2 v_5 + \sqrt{3} a_i c_i v_6 + \sqrt{2} b_i c_i v_7 \right\} \right]^2 \\
 G_{2x}^1 &= \sum_{i=2,6} \frac{t_{1i}}{E_i - E_1} + \sum_{j=3,5} \frac{u_{1j}}{E_j - E_1} \\
 G_{2x}^2 &= \sum_{i=1,6} \frac{t_{2i}}{E_i - E_2} + \sum_{j=3,5} \frac{u_{2j}}{E_j - E_2} \\
 G_{2x}^3 &= \sum_{i=1,2,6} \frac{u_{i3}}{E_i - E_3} + \frac{v_3}{E_4 - E_3} \\
 G_{2x}^4 &= \sum_{i=3,5} \frac{v_j}{E_j - E_4} \\
 G_{2x}^5 &= \sum_{i=1,2,6} \frac{u_{i5}}{E_i - E_5} + \frac{v_5}{E_4 - E_5} \\
 G_{2x}^6 &= \sum_{i=1,2} \frac{t_{i6}}{E_i - E_6} + \sum_{j=3,5} \frac{u_{6j}}{E_j - E_6} \\
 S_{ii} &= 2 [ \alpha \kappa_{||} (a_i a_i - c_i c_i) + (3a_i a_i + b_i b_i - c_i c_i) ]^2 \\
 t_{ii} &= 2 \left[ -\frac{\alpha' \kappa_{\perp}}{\sqrt{2}} (b_i c_i + b_i c_i) + (\sqrt{3} a_i c_i + 2b_i b_i + \sqrt{3} a_i c_i) \right]^2 \\
 u_{ij} &= 2 \left[ -\frac{\alpha' \kappa_{\perp}}{\sqrt{2}} (a_i a_j + b_i b_j) + (\sqrt{3} a_j b_i + 2b_j c_i) \right]^2 \\
 v_j &= 2 \left[ -\frac{\alpha' \kappa_{\perp}}{\sqrt{2}} a_j + \sqrt{3} b_j \right]^2
 \end{aligned} \quad \dots (9)$$

$$\begin{aligned}
 S_{ii} &= 2 [ \alpha \kappa_{||} (a_i a_i - c_i c_i) + (3a_i a_i + b_i b_i - c_i c_i) ]^2 \\
 t_{ii} &= 2 \left[ -\frac{\alpha' \kappa_{\perp}}{\sqrt{2}} (b_i c_i + b_i c_i) + (\sqrt{3} a_i c_i + 2b_i b_i + \sqrt{3} a_i c_i) \right]^2 \\
 u_{ij} &= 2 \left[ -\frac{\alpha' \kappa_{\perp}}{\sqrt{2}} (a_i a_j + b_i b_j) + (\sqrt{3} a_j b_i + 2b_j c_i) \right]^2 \\
 v_j &= 2 \left[ -\frac{\alpha' \kappa_{\perp}}{\sqrt{2}} a_j + \sqrt{3} b_j \right]^2
 \end{aligned} \quad \dots (10)$$

$v$ 's are as given by Abragam and Pryce (1951, page—182 eqn. 4.7)

## DISCUSSION OF EXPERIMENTAL RESULTS

 (a) *g*-values

It is not possible in the present instance to decide *a priori* from the *g*-values the sign of  $\Delta$ , without exhaustive trial and error fitting of susceptibility and anisotropy data, since for both positive or negative signs the ground energy level  $\phi_{1\pm}$  remains unaltered. With  $\Delta$  positive the next higher energy levels of sufficient importance are  $\phi_{2\pm}$ ,  $\phi_{3\pm}$ ,  $\phi_{4\pm}$ ,  $\phi_{5\pm}$  and  $\phi_{6\pm}$  in ascending order of energy, whereas, with  $\Delta$  negative these are  $\phi_{3\pm}$ ,  $\phi_{2\pm}$ ,  $\phi_{6\pm}$ ,  $\phi_{5\pm}$  and  $\phi_{4\pm}$ . For  $\text{CoSiF}_6 \cdot 6\text{H}_2\text{O}$  absorption bands have been observed at  $21000\text{ cm}^{-1}$  and  $18800\text{ cm}^{-1}$  which have been assigned to the transitions  ${}^4\text{T}_1(\text{F}) \rightarrow {}^4\text{A}_2$  and  ${}^4\text{T}_1(\text{F}) \rightarrow {}^4\text{T}_1(\text{P})$  (Abragam and Pryce 1951). It has been found that in order to fit both the experimental susceptibility and anisotropy values for the salts, with a reasonable set of parameters (see Table I) in the given range of temperatures, consistent with the above spectroscopic data,  $\Delta$  must be positive. For this, the energy level scheme is as given in equation (5) in correct order of increasing magnitude. The *g*-values are given by :

$$\left. \begin{aligned} g_{\parallel} &= 2\{2\alpha k_{\parallel}(a^2 - c^2) + 3a^2 + b^2 + c^2\} \\ g_{\perp} &= 2\{-\sqrt{2bca'}k_{\perp} + 2\sqrt{3ac} + 2b^2\} \end{aligned} \right\} \dots (11)$$

Bleaney and Ingram's (1951) experiment at  $20.4^\circ\text{K}$  on  $\text{CoSiF}_6 \cdot 6\text{H}_2\text{O}$  diluted with  $\text{ZnSiF}_6 \cdot 6\text{H}_2\text{O}$  yields four sets of  $g_{\parallel}$  and  $g_{\perp}$  values

	$g_{\parallel}$	$g_{\perp}$
Main transition	5.80	3.44
Subsidiary transitions	6.60	2.62
	6.60	2.82
	3.58	4.09

Since the intensity of the lines of subsidiary groups remain unchanged due to further lowering of temperature, Abragam and Pryce (1951) interpret the extra lines to be due to the ground states of inequivalent cobalt ions situated at different lattice points, where crystal field was different in magnitude. The *g*-values at room temperature cannot be measured owing to very small spin lattice relaxation time. It is very interesting to note in this connection, that the *undiluted* salt  $\text{CoSiF}_6 \cdot 6\text{H}_2\text{O}$  shows a sharp break in the magnetic anisotropy and susceptibility curves in the liquid oxygen range at  $255^\circ\text{K}$  (Mazumdar and Datta, 1964). The crystals which are uniaxial above the transition temperature, start showing orthorhombic symmetry below that temperature. The transition is reversible with temperature except for a small thermal hysteresis loop formed in the region of  $250^\circ\text{K}$ — $260^\circ\text{K}$ . Repeated rapid cooling and heating in this region produces shattering and opacity of the crystal. The absorption spectra of this salt observed here (Mazumdar *et al* 1964) shows the incidence of two new peaks at  $20600$

$\text{cm}^{-1}$  and  $22200 \text{ cm}^{-1}$  below transition temperature in addition to the normal peaks at  $21000 \text{ cm}^{-1}$  and  $19800 \text{ cm}^{-1}$ . X-ray findings by one of our colleagues (Ray, 1964) are very interesting and show the simultaneous existence of a new pseudo-trigonal phase below  $250^\circ\text{K}$ , along with the original trigonal phase, retaining the original trigonal axis as common axis of both these phases. All these appear to indicate a change in phase of the crystal accompanied by possible change of symmetry of the crystal field. These detailed results are being published separately elsewhere. It will be found that  $g$ -values calculated from susceptibility at  $300^\circ\text{K}$  of the undiluted salt is close to those of the main phase of the diluted at  $20^\circ\text{K}$ , whereas at  $20^\circ\text{K}$  the values for the undiluted salt is close to those of the first two subsidiary phases of the diluted salt. Of course, the calculation for the undiluted salt from susceptibility can give only the average value of coexisting phases if any. More investigations on these salts are necessary to clarify the apparent similarity in transition behaviours in them.

(b) *Mean susceptibility and anisotropy values :*

Since a change in phase of the undiluted crystal occurs below  $255^\circ\text{K}$  and we lack as yet detailed structural data for the new coexisting phase apparently having orthorhombic magnetic symmetry, it would be difficult to give exact theoretical calculation of the field parameters to fit exactly the experimental observations. However, since the development of orthorhombicity is only about 5% of the original anisotropy and the original trigonal axis is still the main anisotropy axis of both the phases (Ray—1964), we may limit our discussions to an approximation which considers the mixed phase as a single crystal with trigonal symmetry. In other words, we may neglect the small orthorhombicity normal to the original trigonal axis developed below  $255^\circ\text{K}$ . The break in the susceptibility curve would then correspond to a large sudden change in the trigonal field separation  $\Delta$ , with the reservation inherent in the present approximation. However, in treating one of the coauthor's (Jackson) value of susceptibilities (measured at Bristol) taken at wide gaps of temperatures we cannot pay attention even to this break in the curve and for the present have to average out the variation through the temperature of transition. Fitting the theoretical parameters  $\Delta$ ,  $\alpha\zeta_{||}$ ,  $\alpha'\zeta_{\perp}$  and  $\alpha k_{||}$ ,  $\alpha'k_{\perp}$  by exhaustive trial and error with the mean susceptibility and anisotropy as usual, consistently with the optical absorption levels (Mazumdar *et al.*, 1964) we had to increase the trigonal field coefficient  $\Delta$  from a value of  $830 \text{ cm}^{-1}$  at  $1.67^\circ\text{K}$  to  $952 \text{ cm}^{-1}$  at  $90^\circ\text{K}$  and then decrease it to  $560 \text{ cm}^{-1}$  at  $290^\circ\text{K}$ ; the values for the other parameters which are considered as temperature independent to a first approximation are as given in the Table I.  $\alpha$ 's,  $\zeta$ 's and  $\kappa$ 's cannot be independently calculated owing to the product forms in which they appear in the equations.

In spite of the approximations involved the major fact about the anisotropic reduction of spin-orbit coupling due to  $3d$ -charge overlap with  $s$ - and  $p$ -ligand



charge clouds, and the general variation in  $\Delta$  with temperature due to lattice expansion and relaxation effects are prominently brought out in  $\text{Co}^{2+}$  fluosilicate. Without more structural data it is not possible to say whether the tendency for a maximum value of  $\Delta$  in the region of  $90^\circ\text{K}$  for the salt, is connected entirely with the phase transition or not, though this is very likely as indicated by the detailed anisotropy data in the liquid oxygen range taken by some of our co-workers to be published elsewhere.

TABLE I

Temperature variation of effective mean moment  $(\mu_{\text{eff}})$  and anisotropy  $(p_{\parallel}^2 - p_{\perp}^2)$  of  $\text{CoSiF}_6 \cdot 6\text{H}_2\text{O}$

Temp $^\circ\text{K}$	$\Delta\text{cm}^{-1}$	$p_{\parallel}^2 - p_{\perp}^2$	$\overline{p^2}$	$g$ -values
290.4	525	10.06 (10.05)	25.06 (25.10)	$\left\{ \begin{array}{l} g_{\parallel} = 5.98 \\ \quad (5.80) \\ g_{\perp} = 3.37 \\ \quad (3.44) \end{array} \right.$
90.1	950	31.38 (31.34)	22.16 (22.19)	$\left\{ \begin{array}{l} g_{\parallel} = 6.90 \\ \quad (5.80) \\ \quad (6.6) \\ g_{\perp} = 2.42 \\ \quad (3.44) \\ \quad (2.62) \end{array} \right.$
20.4	880	33.81 (33.92)	17.62 (17.53)	
4.2	840	30.19 (30.25)	15.06 (15.06)	
1.67	830	29.60 (29.67)	14.60 (14.54)	

$$P_{\parallel} = \alpha\zeta_{\parallel} = -170\text{cm}^{-1}$$

$$Q_{\parallel} = \alpha\kappa_{\parallel} = 1.21$$

$$P_{\perp} = \alpha'\zeta_{\perp} = -194\text{cm}^{-1}$$

$$Q_{\perp} = \alpha'\kappa_{\perp} = 1.39$$

Values in parentheses are the experimental values. Those for  $g$ 's within parantheses are for the diluted salt (Bleaney *et al*, 1951).

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